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THE CORROSION OF ZrO_2 LAYERS OBSERVED BY AFM

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ABSTRACT: Coatings prepared by sol-gel method are widely utilizable in various areas. What is found to be very attractive is their application as protective coatings. Coatings of ZrO_2 provide very environmental resistance. We studied water resistance of ZrO_2 coatings for better understanding of corrosion processes. ZrO_2 coatings were prepared on microscope slide glasses by dip-coating method from sols. Corrosion has been investigated as a topographic change of surface coatings after theirs boiling for 2 hours in distilled water and 1 hour in NaOH solution (1 mol/dm^3). Surface's topography was observed by AFM. We found out that the "knolls" shapes arise on ZrO_2 surface as a consequence of corrosion. These shapes probably arise from the products of corrosion.

KEY WORDS: ZrO_2 coatings, sol-gel, corrosion, AFM

1. INTRODUCTION

One of the most common problems at the industrial level is material's damage due to corrosion. Certainly, corrosion cannot be avoided, but it can be delayed by using corrosion inhibitors, protective coatings or by new materials [1].

Sol-gel layers prepared on the surface of materials favourably affect properties of the substrate, thus expanding the possibilities of utilizing glass in optics, communication technology, electronics and other additional fields of technology. Inorganic sol-gel layers may also be used in order to protect the surface from the effects of aggressive solutions. Their performance in this respect depends primarily on their chemical composition, porosity and thickness of the layer. Layers containing TiO_2, ZrO_2 and SiO_2 exhibit very good resistance to atmospheric effects and to chemical effects [2]. ZrO_2 is characterized by extreme thermal, chemical and mechanical stability which, together with its optical and electrical properties, gives a rise to a wide range of technical applications for ZrO_2 thin films and coatings, especially in optics, electronics and protective applications [3].

Atomic force microscope (AFM) has proven to be essentially valuable tool for investigation of glass surfaces and surfaces of coatings [4]. The crystallization and the corrosion mechanisms of TiO_2 coatings on glass substrates were recently studied, and it was demonstrated that atomic force microscopy (AFM) is ideally suited for such an investigation [5]. Atomic force microscopy (AFM) is a complex instrument used to investigate the surface at the micro- and nanometer scale [6,7].

This work deals with the study of morphology and topography of ZrO_2 layers prepared by using sol-gel method before and after corrosion in water and in alkalic solution.

2. EXPERIMENT

Thin layers were applied to microscope slide glasses by using dip-coating method, and by using drawing speed of 90 mm/min. Layers were dried at 80 °C and consequently fired at 450 °C with burning speed of 10 °C/min. Thickness of obtained layers was 40 nm. Tests of ZrO_2 thin layer's chemical durability were carried out either in boiling distillery water for 2 hours or by using alkaline solutions of NaOH (1 mol/dm^3) and boiling for 1 hour.

3. RESULTS AND DISCUSSION

3.1 Topography of layers

Measurements were performed with AFM apparatus (NT-206) operating in the air ambient conditions. Sample topography was taken by scanning in static mode using Mikro-Masch silicon cantilevers CSC38/AlBS with spring force constant k = 0.03 N/m. Images made with raster of 256×256 in the scale of 5×5 μm. 2D, 3D and profile of studied layers are shown in Fig. 1.

During measuring of surface topography by using AFM, we determined values of unevenness height at particular points on surface. As the output of measuring we got the set of uneven height values that had to be processed in an appropriate manner. We have used following process. Acquired height values were adapted, so that in the direction of quick scanning they have been associated to straight line going through two lowest values for particular scan. Same adaptation was subsequently made in the direction of slow scanning. These adaptations allow acquirement of image of the surface, which corresponds the most to reality for randomly chosen rough surfaces. These values were then associated to the lowest point of the image placed at zero position. Set of height values (z_{ij}) acquired in such a way served for calculation of values describing layer properties for particular images and these are [8,9]:

1). Mean $\overline{z}$ of measured height values z_{ij}:

$$\overline{z} = \frac{1}{n.m}\sum_{i=1}^{n}\sum_{j=1}^{m} z_{ij} \tag{1}$$

Mean value $\overline{z}$ characterizes heights z_{ij} associated to the lowest point of the processed AFM image.

2). Standard deviation σ of measured values z_{ij} around $\overline{z}$:

$$\sigma = \sqrt{\frac{1}{n.m}\sum_{i=1}^{n}\sum_{j=1}^{m}(z_{ij} - \overline{z}^2)} \tag{2}$$

Values of standard deviation σ of measured heights z_{ij} characterize roughness of particular surface. This is usually labelled as rms – roughness in literature.

3). The interquartil range is the difference between 75th and 25th percentile of the data. Since only the middle 50 % of the data affects this measure, it is robust to outliers.

Statistical characteristics of layers are presented in Tab. 1.

Fig. 1 shows that presence of lowered, cratered places with approximately round diameters is characteristic for uncorroded layer of ZrO_2. These positions can be considered to be pores. We also observe presence of protuberances randomly distributed on the surface. After corrosion in water, we do not observe lowered cratered places anymore and also protuberances are scarcer. After corrosion in NaOH we observe higher protuberances randomly distributed on the surface. We do not observe pores anymore.

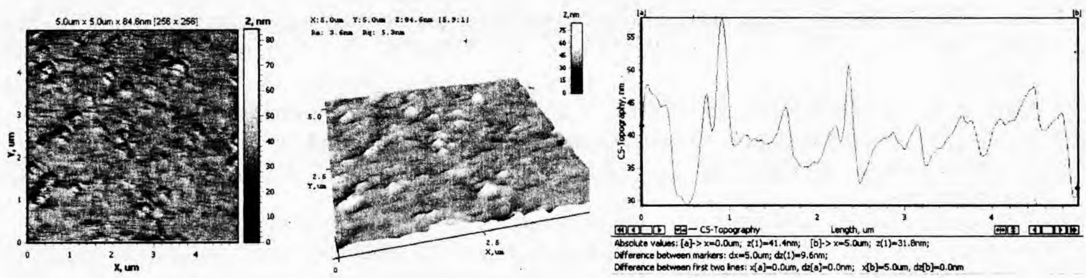
Assessment of corrosive environment's influence on ZrO_2 layer can be done by comparing statistical characteristics of this layer before and after corrosion. In order to obtaine this assessment, we have used means of layer heights, roughness (standard deviation) and interquartile range.

When comparing average values (Tab. 1), we observe that mean of layer heights corroded in water (24.41 nm) is almost twice as low as mean of uncorroded layer heights (40.10 nm). Mean of layer heights corroded in NaOH (40.10 nm) is approximately for one fourth higher than mean of uncorroded layer heights (51.86 nm).

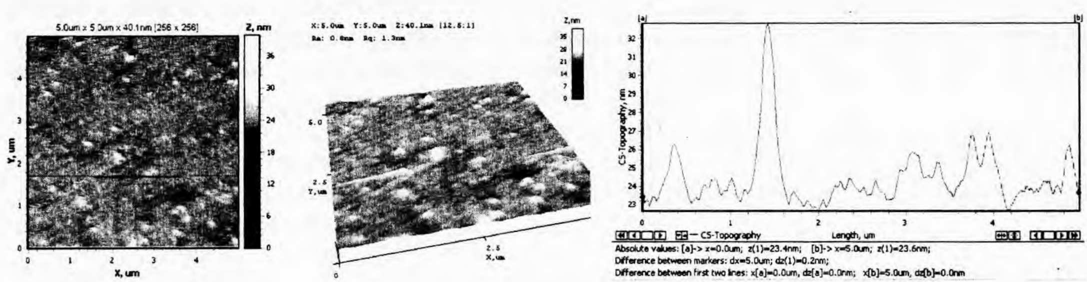
Same dependence can also be observed at standard deviation characterizing roughness and also at interquartile range (Tab. 1).

Tab. 1: Statistical characteristics of layers

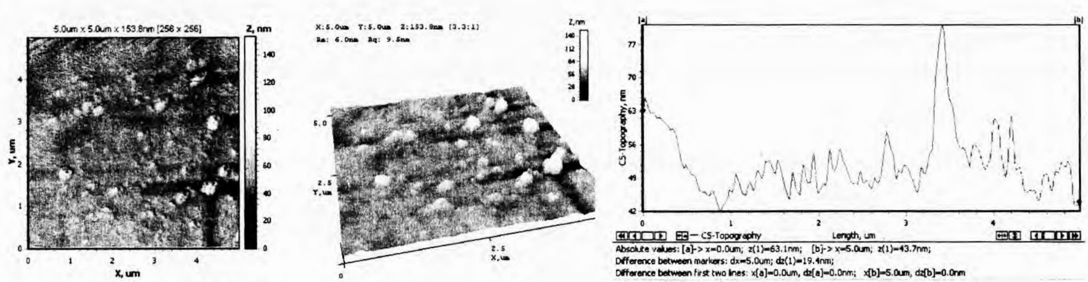
	Average / nm	**Roughness / nm (standard deviation)**	**Interquartile range / nm**
uncorroded layer	40.10	5.33	4.78
aqua-corroded layer	24.41	1.28	1.03
alkaline-corroded layer	51.86	9.54	7.90



uncorroded layer



aqua-corroded layer



alkaline-corroded layer

Fig. 1: 2D, 3D and profile of studied layers

4. CONCLUSIONS

Results imply that corrosion of ZrO_2 layer in water induces significant decrease of surface roughness, while corrosion in NaOH induces significant roughness increase of ZrO_2 layer surface.

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5. REFERENCES

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